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INFRARED SPECTRA OF HF-DF MIXED CRYSTALS

AND THE STRUCTURE OF HYDROGEN FLUORIDE

by

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ABSTRACT

The infrared spectra of HF-DF mixed crystals have been studied throughout the composition range. Unlike HF, the spectrum of pure DF shows only the two peaks in the stretching region which are characteristic of the zig-zag chain structure found by X-ray studies for HF and spectroscopically for HCl and HBr. The spectrum of pure HF shows the anomalous features previously reported . From the mixed crystal spectra it is clear that there is only one kind of site and one kind of strongly interacting pair in either HF or DF. A resolved peak due to triplets of HF (in DF) and of DF (in HF) has been observed. It is concluded that the extra peaks in pure HF probably arise from lattice combinations; in any case all of the major features of the spectra are accounted for by the zig-zag chain structure of symmetry D_{2h}^{16}-Pmnb. It has not yet been possible to interpret the lattice spectrum in detail.

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According to the x-ray structure determination of Atoji and Lipscomb[1]

1. M. Atoji and W.N. Lipscomb, Acta Cryst. 7, 173 (1954).

crystalline HF is constructed from zig-zag hydrogen bonded chains, the

structure being similar, perhaps identical, with that previously deduced

for HCl and HBr from their infrared and Raman spectra[2].   However, the in-

2. D.F. Hornig and W.E. Osberg, J. Chem. Phys. 23, 662 (1955).

frared absorption spectrum of crystalline HF reported by Giguere and

Zengin[3] had features which seemed incompatible with the x-ray crystal

3. P.A. Giguere and N. Zengin, Can. J. Chem. 36, 1013 (1958).

structure and that were at variance with the well understood spectra of

crystalline HCl and HBr. It seemed important, therefore, to clarify this

question.

Atoji and Lipscomb found that HF crystallized in an orthorhombic

structure of space group D_{2h}^{17}-Bmmb with four molecules in the unit cell.

It is built from infinite zig-zag chains of hydrogen bonds in parallel

planes, with an FH...F distance of 2.49 $\pm$ .01 $\overset{o}{A}$ and a hydrogen bond angle

about the fluorine of 120.1°. The hydrogen atoms were not definitely

located but their position seemed statistical, so that individual chains might point in either direction. However, in a footnote it was indicated that almost as good agreement is found with the ordered structure, D_{2h}^{16}-Pmnb, which has the same features otherwise.

An infinite zig-zag chain should give rise to two spectroscopically active vibration frequencies; when two such chains are coupled weakly, each of the two should be doubled in turn. For the ordered structure, D_{2h}^{16}, two of the resulting four lines should appear in the infrared spectrum and the remaining two should appear at nearly the same frequencies in the Raman spectrum. For the D_{2h}^{17} structure, assuming order within the chains but randomness in the chain directions, the coupling between chains would simply broaden the pair of lines.

What was observed by Giguère and Zengin was a pair of strong lines at 3060 cm^{-1} and 3420 cm^{-1} and two weaker lines at 3270 cm^{-1} and 3590 cm^{-1}. They advanced the opinion that the two weak bands were the Raman components which had become weakly active, perhaps as a result of the disorder. If this interpretation were correct the presence of four nearly equally spaced lines (rather than two closely spaced pairs) would imply that the forces between molecules in separate chains were nearly as great as the forces between molecules in a chain. They found that to fit the four frequencies they needed two strong interaction constants between neighbors, 0.65×10^5 dynes/cm. and 0.36×10^5 dynes/cm. Such a conclusion is quite incompatible with the x-ray evidence but it seems to be supported by the richness of the low frequency spectrum in the librational region. Here the x-ray structure predicts three infrared active lines,

whereas no less than four were reported by Giguère and Zengin.

There was every reason on our part to believe in the reliability of the infrared spectra reported since we had available independent spectra which had been taken by Dr. G.L. Hiebert[4] in 1954 but which had not been

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4. G.L. Hiebert, Private Communication.
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published because he had not been able to resolve precisely the questions raised by Giguère and Zengin. Hiebert's spectrum is given in Fig. 1, both in the high and low frequency regions.

It seemed possible to clarify these questions by studying the spectra of deuterated and partially deuterated crystals. For example, if a very small number of HF molecules are included in a DF crystal (or DF in HF), one observes the spectrum of an isolated, uncoupled molecule in the field of the host lattice. If there is only a single site (i.e., if the four molecules in the unit cell are symmetrically equivalent) only a single peak would be observed. The presence of multiple peaks would indicate the presence of non-equivalent sites in the host lattice. When the concentration of solvent molecules is increased, solvent pairs occur and the two peaked pattern arising from the coupled motions should be observed. According to the x-ray structure only pairs consisting of adjacent molecules in a chain should be observed whereas if the Giguère and Zengin suggestion is correct there are at least two strong interactions and two different pair spectra should be found.

These principles have been found fruitful in the study of other hydrogen halides[5], of ice[6] and of hydrate crystals[7]. We therefore undertook

5. D.F. Hornig and G.L. Hiebert, J. Chem. Phys. 27, 752 (1957).
6. C. Haas and D.F. Hornig, J. Chem. Phys. 32, 1763 (1960).
7. J. Schiffer, Ph.D. Thesis, Princeton University, 1962.

to study the infrared spectra of DF and of mixed HF-DF crystals.

Experimental Technique

The technique employed for the preparation of DF was to deuterate KHF_2 with heavy water and then to decompose, by strong heating, the resulting KDF_2 into KF and DF. The KHF_2 was obtained commercially and had a stated purity of 99.7 %. The main impurities were 0.26 % KF, 0.02 % K_2SiF_6 and 0.02 % Cl. The generation of the DF and HF gases was carried out in an evacuated copper system consisting essentially of a heating vessel and a condenser. As potassium bifluoride is hygroscopic, the gases generated in the initial stages of heating the substance were purged and only the gases produced in the later stages of heating were collected for use in the experiments. A column of copper filings prevented entrainment of the decomposition product KF by the gases into the condenser. The sample gases were prepared in small quantities afresh for each experimental run. Mixtures of KHF_2 and KDF_2 yielded mixtures of HF and DF gases. However, the percentage compositions indicated on the spectra (Fig. 2) were estimated from the relative intensities of the HF and DF portions of each spectrum, noting that the absorption coefficient per molecule of HF is twice that of DF.

The low temperature cell used was similar to that described in the literature[8] but was constructed entirely of copper metal tubing. The

8. E.L. Wagner and D.F. Hornig, J. Chem. Phys. 18, 296 (1950).

windows of the cell and the backing plate on which gases were condensed
to form crystalline films were of AgCl except that, for recording spectra
beyond 25µ, CSI was used. There was no trace of attack of the AgCl back-
ing plate by the hydrogen fluoride gas even after several experimental
runs. CSI was, however, protected by a covering of a thin film of poly-
ethylene which has good transmission characteristics up to 40µ. A teflon
tube was found to be convenient to connect the gas reservoir with the low
temperature cell. By opening a needle valve on the gas reservoir the
gases were admitted into the low temperature cell in a controlled manner
and were allowed to impinge on the precooled backing plate to form crys-
talline films. The backing plate was cooled by keeping it in good con-
tact with a copper block which was directly in contact with liquid
nitrogen. The temperature of the crystalline films was not measured di-
rectly but was estimated to be close to $-190^{\circ}C$.

The spectra were recorded with a Perkin-Elmer Model 12B Spectrometer,
modified for use as a ratio-recording double-beam instrument[9], with LiF,

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9. D.F. Hornig, G.E. Hyde and W.A. Adcock, J. Opt. Soc. Am. 40, 497
    (1950).

NaCl, KBr and KRS-5 prisms covering approximately the region from 1.5 to
30µ.

Results

The spectra of the stretching region of films of various HF-DF com-
positions are shown in Fig. 2. Spectra shown in juxtaposition in the HF
and DF regions were obtained on the same film. The frequencies of the
various peaks are listed in Table 1 and those for the pure crystal are

compared with those of previous investigators in Table 2. The small deviations in the frequency values of the four pure HF peaks from the three sources could very well be due to the uncertainties in locating the absorption maxima of the rather broad bands.

The general picture obtained is clear. The dilute spectra show only a single sharp peak at 3273 cm^{-1} (width at half-height 55 cm^{-1}) in HF and 2404 cm^{-1} (width, 40 cm^{-1}) in DF. Hence we conclude that all HF (or DF) sites are equivalent. The 7-10 ^{O}/o spectra show a pair of doublet peaks on either side of the singlet peak. We shall discuss this at more length later but this fact alone is enough to say that there is only one kind of pair, presumably adjacent molecules in a chain, which interact strongly.

As the concentration increases further, triplets and longer chains of molecules of a single isotopic species occur. The central singlet peak decreases in intensity while the wings broaden and develop new structure. Except for the fact that more structure is resolvable most of the pattern follows closely what was found in the HCl-DCl and HBr-DBr systems. However, since the splitting due to coupling in the chain should not exceed twice that from pairs, it is plain that the new peaks which appear at 3470 cm^{-1} and 3570-3585 cm^{-1} in HF, or at 2705 cm^{-1} in DF are not part of the pattern arising from the superposition of chain spectra.

The spectrum of pure HF is essentially identical with those obtained by Hiebert and by Giguère and Zengin. However, that of pure DF shows only the two peaks expected from the x-ray structure and gives no hint of any anomaly. Hence either the problem of HF is one of interpretation, i.e., that the two weaker peaks are not fundamental vibrations, or the structures of HF and DF are different. The latter does not seem likely since

the singlet and pair spectra of dilute DF in HF, which reflect the ~~HCl~~ HF

structure, show no anomalous features.

Altogether, the qualitative features of the spectrum suggest strong-
ly that the x-ray structure is correct and that both HF and DF are con-
structed from zig-zag chains in parallel planes. Nevertheless, there are
at least three quantitative problems which need further discussion: (1)
According to the simple theory the singlet line should lie at the mean of
the two pair lines. In fact there is a small displacement in both HF and
DF. (2) The singlet line is usually expected to occur at the mean of the
two lines in the pure compound. This is the case in DF but in HF the mean
of the two strong lines is some 35 cm^{-1} lower than the singlet frequency.
This would usually be taken to indicate that there are more fundamental
frequencies. However, the average of the four lines in pure HF is some
60 cm^{-1} above the singlet and even the mean of the lower three components
is some 25 cm^{-1} below so that inclusion of the weak lines as fundamentals
does not help matters. (3) The frequency separation of the two peaks in
the pure crystal should be twice that in the pair spectrum. This is the
case for pure DF but in HF the pure crystal splitting is 354 cm^{-1} while
twice the pair splitting is only 324 cm^{-1}. Consequently, although almost
everything seems to fit the x-ray structure, there are quantitative diffi-
culties and the pure HF spectrum seems distinctly anomalous.

The spectra of the lattice vibrations of HF and DF (97.6 $^o/o$) are
shown in Fig. 3. No consideration should be given to the relative inten-
sities of bands studied with different prisms since samples of different
thickness were employed in each region. The frequencies of the absorp-
tion maxima, together with those obtained by earlier workers, are recorded

in Table 2. The spectra obtained in the three studies differ markedly.
In that of Giguère and Zengin the sharp peak at 547 cm^{-1} is easily the
most intense in the spectrum, with a broad shoulder running from 600 to
800 cm^{-1}, while in the Hiebert spectrum the sharp peak at 550 cm^{-1} seems
less intense than the well resolved band at 730 cm^{-1} although the film
is too thick to be certain. Our own spectra are more comparable to
Hiebert's in that a band at 790 cm^{-1} is well resolved, although we have
no comparative intensities because the two peaks were observed on films
of different thickness. The weak peak at 515 cm^{-1} in our spectrum does
not appear in Hiebert's and is only suggested by a shoulder in that of
Giguère and Zengin. Altogether, it seems that some or all of the spectra
may be marred by impurities, of which ice condensed on the cell window
may be the most probable. Ice has an extremely strong absorption band at
about 800 cm^{-1} and a weak subsidiary peak at 520 cm^{-1}, for example.

In any case, the shift in going from the HF to the DF spectrum demon-
strates that the peaks at 1200 cm^{-1}, 971 cm^{-1}, 790 cm^{-1} and 555 cm^{-1} are
all primarily proton motions. Even the 370 cm^{-1} peak, ascribed to a
lattice translation by Giguère, is shifted to a value below 350 cm^{-1}, the
lower limit of our observations, so that it must be strongly coupled to
the librations.

It does not seem likely, on the basis of the available spectra, that
the low frequency region can provide any definitive information.

Discussion

It was pointed out previously that the singlet peak is not centered
between the pair peaks in either HF or DF, being high in the former and

low in the latter case. This suggests an interaction with the host lattice. To get an idea of the magnitude of the interaction let us consider the situation

$$A - F \quad B - F \quad A - F \quad ,$$

where all of the molecules have a principal force constant f and the nearest neighbor interaction constant is f'. If we are considering the root nearest the isolated $B - F$ frequency, $\lambda^o_B = f/\mu_B$, where μ_B is the reduced mass of $B - F$, the secular determinant is, to a good approximation,

so that

$$\begin{vmatrix} f(1 - \dfrac{\mu_A}{\mu_B}) & f' & 0 \\ \\ f' & f - \lambda\mu_B & f' \\ \\ 0 & f' & f(1 - \dfrac{\mu_A}{\mu_B}) \end{vmatrix} = 0 \qquad (1)$$

$$\lambda^s_B = \lambda^o_B - \frac{2f'^2}{\mu_B f (1 - \mu_A/\mu_B)} \qquad (2)$$

or

$$\frac{\lambda^S_B - \lambda^o_B}{\lambda^o_B} = \frac{2(v^S_B - v^o_B)}{v^o_B} = \frac{2f'^2}{(\dfrac{\mu_A}{\mu_B} - 1)f^2} \qquad (3)$$

However, the splitting, Δv^P_B, of an isolated pair of $B - F$ molecules is easily seen to be

$$\frac{\Delta v^P_B}{v^o_B} = \frac{f'}{f} \qquad (4)$$

so that

$$v_B^S - v_B^O = v_B^O \times \left(\frac{\Delta v_B^P}{v_B^O}\right)^2 \frac{1}{\left(\frac{\mu_A}{\mu_B} - 1\right)} \tag{5}$$

In equation (5) v_B^S is the singlet frequency and v_B^O is the frequency of an isolated B - F molecule. In the present case, then, if B = H and A = D, we have $\Delta v_H^P = 162 \text{ cm}^{-1}$ (the mean of the 7 °/o and 22 °/o curves) and $v_B^O = 3273 \text{ cm}^{-1}$ (to a sufficient approximation). Therefore

$$v_H^S - v_H^O = 3273\left(\frac{162}{3273}\right)^2 \frac{1}{0.91}$$

$$= 8.8 \text{ cm}^{-1} \tag{6}$$

Similarly

$$v_D^S - v_D^O = -2404 \left(\frac{120}{2404}\right)^2 \frac{1}{.475}$$

$$= -12.6 \text{ cm}^{-1} \tag{7}$$

The same argument, when applied to the situation A - X B - X B - X A - X leads to the result that:

$$\overline{v_B^P} - v_B^O = (v_B^S - v_B^O)/2 \tag{8}$$

if $\overline{v_B^P}$ is the mean of the pair frequencies. It also shows that the pair splitting of B - F is not changed by coupling to A - F. It should be noted here that these results are not significantly affected if the single A - F molecules are replaced by infinite chains of A - F.

From Equations 6, 7 and 8 we conclude then that

$$v_H^S - \overline{v_H^P} = 4.4 \text{ cm}^{-1}$$

and

$$\nu_D^S - \overline{\nu_D^P} = -6.3 \text{ cm}^{-1}$$

We have, experimentally, from the 7 ^{o}/o and 22 ^{o}/o HF spectra,

$$\nu_H^S - \overline{\nu_H^P} = 3273 \text{ cm}^{-1} - 3265 \text{ cm}^{-1} = 8 \text{ cm}^{-1}$$

and, from the 10 ^{o}/o and 28 ^{o}/o DF spectra,

$$\nu_D^S - \overline{\nu_D^P} = 2402 \text{ cm}^{-1} - 2414 \text{ cm}^{-1} = -12 \text{ cm}^{-1}.$$

The signs and approximate relative magnitudes are certainly correct although the absolute magnitudes are larger than calculated. Using the experimental results, we therefore conclude that

$$\nu_H^O = 3257 \text{ cm}^{-1}; \ \nu_H^S - \nu_H^O = 16 \text{ cm}^{-1}$$

and

$$\nu_D^O = 2426 \text{ cm}^{-1}; \ \nu_D^S - \nu_D^O = -24 \text{ cm}^{-1}.$$

A further check on this interpretation is that triplets should have three frequencies, the high and the low being infrared active and the central one inactive. The splitting of the highest and lowest frequencies is $\Delta\nu_B^T = \sqrt{2}\Delta\nu_B^P$. Also, the position of the mean frequency is (for the same model as used for singlets and pairs):

$$\overline{\nu_B^T} - \nu_B^O = (\nu_B^S - \nu_B^O)/3$$

From the pair splittings, the predicted triplet splittings are therefore 229 cm^{-1} (HF) and 170 cm^{-1} (DF). The predicted positions of the triplet lines are thus:

HF; $3257 + 5 \overset{+}{-} 115 = 3377$ cm^{-1} and 3147 cm^{-1}

DF; $2426 - 8 \overset{+}{-} 85 = 2503$ cm^{-1} and 2333 cm^{-1}

The HF line at 3145 cm^{-1} and the DF line at 2329 cm^{-1} are therefor the triplet lines. Their high frequency counterparts are not resolved in either spectrum.

Up to this point we can conclude that even the fine details of the spectra are quantitatively accounted for by the zig-zag chain model. The situation though is not so clear in the pure crystals.

The zig-zag chain model with 4 molecules per unit cell predicts four fundamental frequencies. Since they belong to four different symmetry species each is proportional to $\mu^{-1/2}$. Consequently the pattern in HF should be the same as in DF, except that all splittings in HF should be greater by a factor 1.38. The average of the four frequencies should be close to the previously defined ν^o but need not be identical since

$$\bar{\lambda} = [f + \Sigma f_1]\mu^{-1} = \lambda^o [1 + \Sigma f_1/f]$$

where the sum is over the interaction constants between a given molecule and the corresponding molecules in all other unit cells. Nevertheless, the ratio of displacements from ν^o should be 1.38. The splittings in the pure crystal would be twice those in a pair if only nearest neighbors in a chain contributed to the interaction constant; if further neighbors contribute this ratio changes and usually increases. Nevertheless, the H-F/D-F ratio should again be 1.38 if all force constants are the same in HF and DF.

The mean of the two HF frequencies in the pure crystal, 3237 cm^{-1},

is 20 cm^{-1} below ν_H^O, while for DF the mean is 2406 cm^{-1}, 20 cm^{-1} below ν_D^O. Their ratio is low but by the nature of the process involved in finding ν_A^O and ν_D^O it may be within experimental error of 1.38.

A serious discrepancy occurs when the HF splitting, 354 cm^{-1}, is compared with that in DF, 243 cm^{-1}. The ratio, 1.46 differs from 1.38 by much more than the experimental error and can only be interpreted to mean that the interaction constant between neighbors is about 10 °/o higher in HF. This would point to a higher polarity and stronger hydrogen bonds in HF than DF. This conclusion is consistent with the fact that the ratio of mean frequencies in the pure crystals, 1.34, is low. The same is true of ν_O^H/ν_O^D where the ratio is the same. This analysis might be pushed a little further but it does not appear fruitful to do so until the Raman frequencies for crystalline HF are known.

One further point seems worth mentioning. In the librational spectrum of a single zig-zag chain, the two molecules may librate either in phase or out of phase, giving rise to two infrared active frequencies for the in-plane libration and one for the out of plane libration. When two such chains are coupled each gives rise to a Raman frequency as well for each infrared active frequency.

The translational lattice spectrum should be similar. The motion in which all molecules translate parallel to the chain has nearly zero frequency. However, the corresponding mode in which the displacements of the two molecules are out of phase may have a frequency in this region and may be infrared active by coupling to the libration and stretch of the same symmetry. Exactly the same analysis applies to translation perpendicular to the chain but in the plane of the zig-zag. However,

the translation perpendicular to the plane and the chain should give no
infrared lines except one of nearly zero frequency.

In sum then, we expect five low frequency lines, three libration
and two translation. These cannot all be the lines observed since
four of them are hydrogen motions, as shown by substitution of deuterium.
In view of the discrepancies between the various spectra, a complete
analysis is presently impossible. There is enough subsidiary structure
in all of the published spectra to suggest that the true situation may
be quite complicated.

Conclusion

On the basis of all of this work one can say with some confidence
that the infrared spectrum of the stretching region is in good accord
with the zig-zag hydrogen bonded chain structure. It appears that the
two extra lines in the pure HF spectrum are either combination bands
with lattice modes or impurity bands. The hydrogen bonds in HF appear
stronger than in DF, a point which could presumably be checked since
it suggests a small difference in the lattice constants.

Table I. Absorption Peaks in the Spectra of HF-DF Crystals

% DF	DF Frequencies (cm^{-1})	HF Frequencies (cm^{-1})	% HF
0.0		3060 3270 3414 3581	100
3.5	2404 (S)	3060 3264 3414 3585	96.5
10	2352 (P) 2402 (S) 2473 (P)	(3060) 3267 3404 3569	90
28	2329 (T) 2355 (P) 2402 (S) 2474 (P)	3096 3178 3267 3402 3571	72
60	2318 2346 2394 2509 2600 (2698)	3132 3180 (P) 3267 (S) 3363 3460	40
78	(2305) 2389 2517 2706	3145 (T) 3181 (P) 3269 (S) 3348 (P) 3470	22
93	2286 2528 2705	3188 (P) 3277 (S) 3345 (P)	7
97.6	2284 2527	3273 (S)	2.4

S - single molecule; P-molecular pairs; T-molecular triplets.

Table II.   Frequencies in the Spectra of Pure HF and DF Crystals

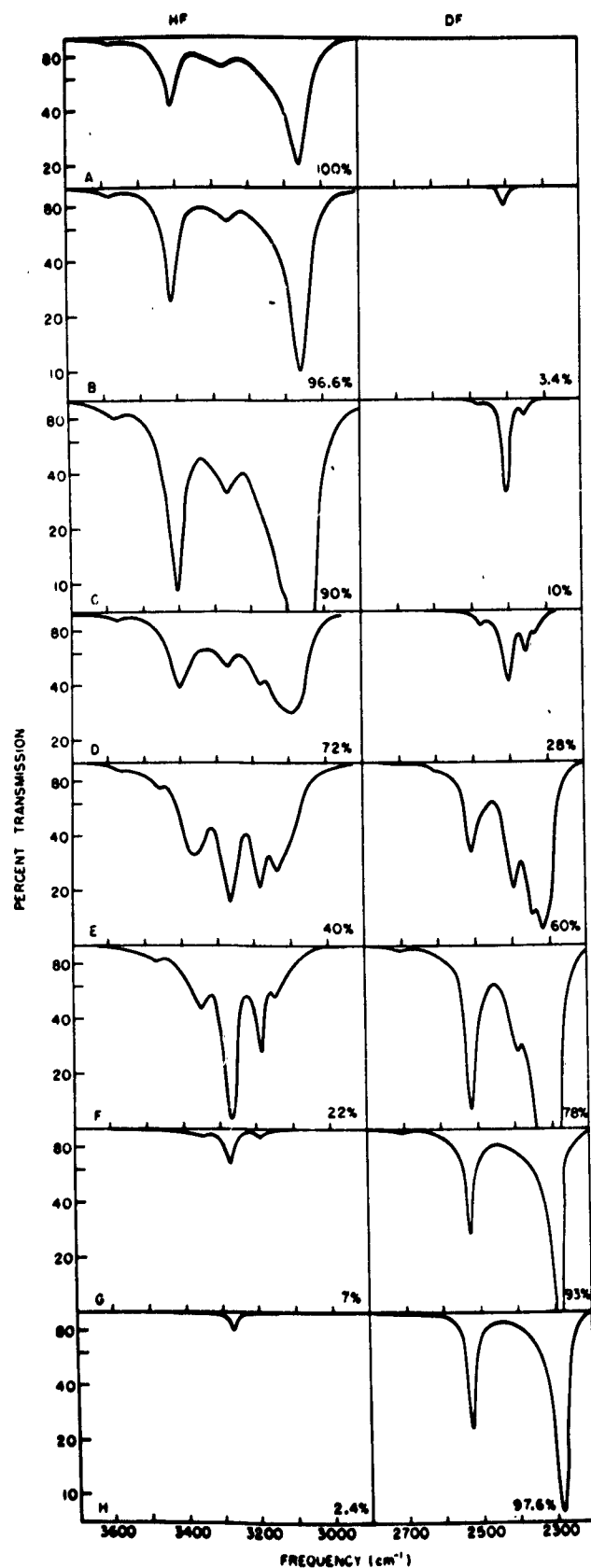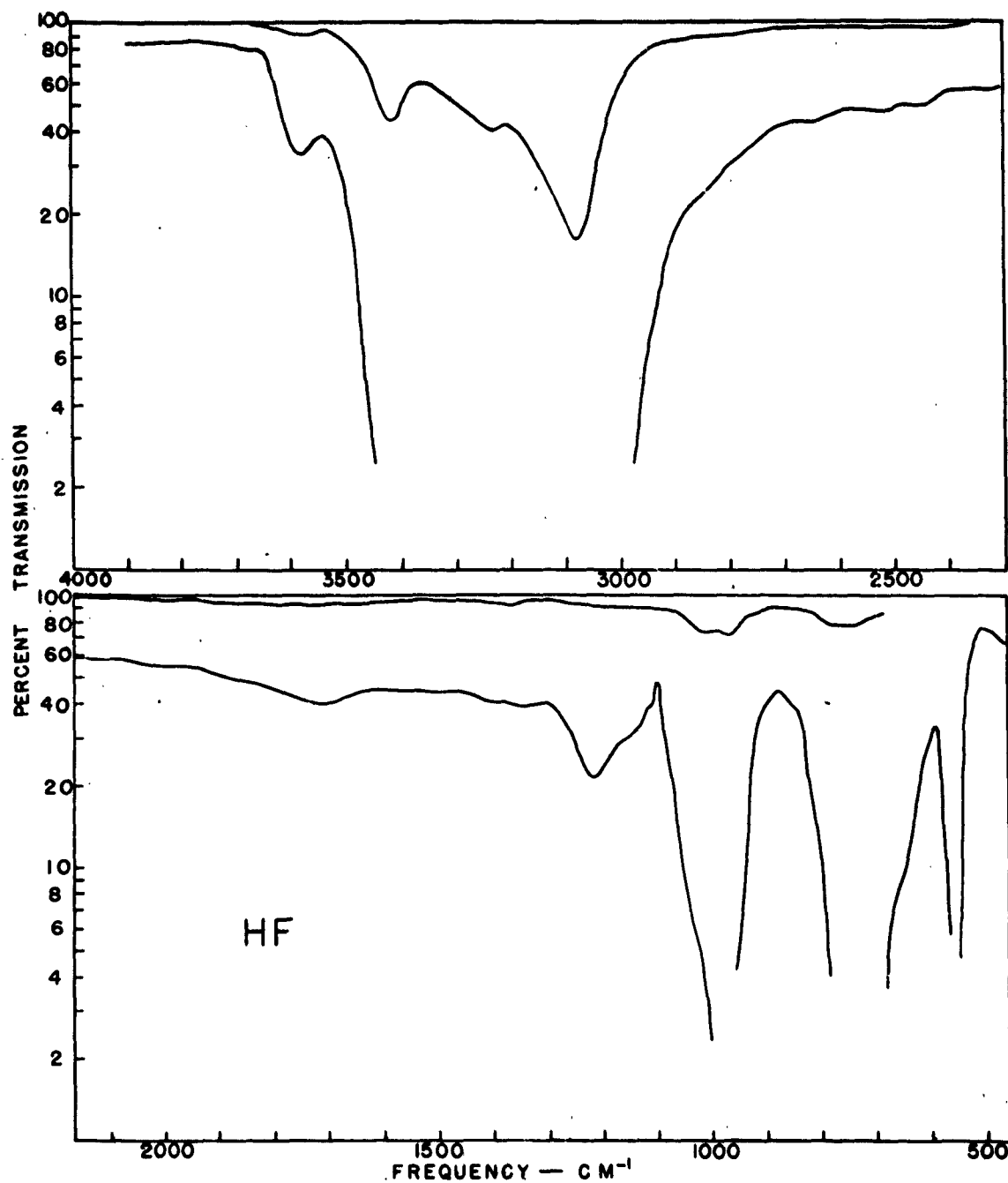| DF Frequencies (cm^{-1})	HF Frequencies (cm^{-1})		
This work	This work	Ref. 3	Ref. 4
	3581	3590	3580
2527	3414	3420	3415
	3270	3270	3232
2284	3060	3060	3080
855	1200	1204	1215
715	971	(955-1010)	1015
			970
570	790		780
			744
405	555	547	558
	515		
	370	366	
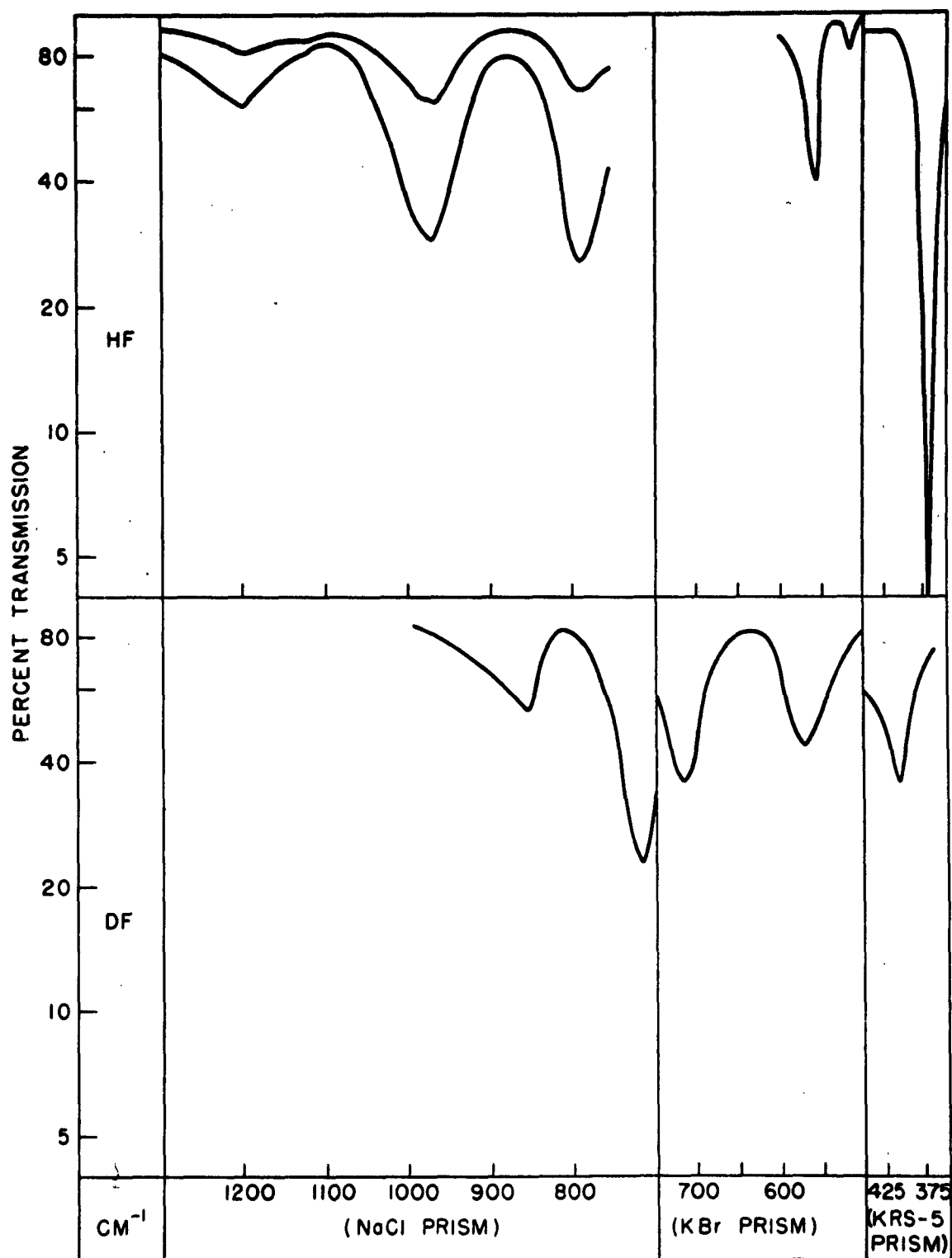
FIG. 3. LATTICE SPECTRA OF HF AND DF CRYSTALS

FIG. 2. SPECTRA OF MIXED HF-DF CRYSTALS

FIG. I INFRARED SPECTRUM OF HF CRYSTAL[4]